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FINAL REPORT

by

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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

Contributions to the following topics have been reported: 1) Torsional Pendulum/Torsional Braid Analysis; 2) Time-Temperature-Transformation (TTT) Cure Diagram; 3) The Glass Transition Temperature (Tg) as an Index for Monitoring Cure; 4) Anomalous Behavior of Thermosetting Polymers: Properties at Room Temperature Vs. Time and Temperature of Cure; 5) Physical Aging of Thermosetting Systems.

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SUMMARY

The following short sections (I-V) summarize the thrust and conclusions of developments which have been supported at least in part by the ONR Contract. Reference numbers [] refer to the numbering of Technical Reports.

I. TORSIONAL PENDULUM/TORSIONAL BRAID ANALYSIS [2,3]

The freely oscillating torsion pendulum (TP), which is the simplest and perhaps the most sensitive dynamic mechanical technique for characterizing polymers, is used in the quantitative mode to provide shear moduli (storage and loss) data of solid specimens vs. temperature or lapsed time. The scope is extended with advantage in the torsional braid analysis (TBA) mode which uses a composite specimen, made simply by impregnating a glass braid substrate with fluid (e.g., a polymer in a volatile solvent). TBA provides information on chemical and physical transformations over a wide range of conditions (e.g., from liquid to solid and vice versa). The TBA technique has been used principally with thermosetting systems. Developments on thermosetting systems which have arisen in our laboratory from using the TBA technique are summarized in the following sections. It is noted that the TBA/TP technique was the first commercially available automated dynamic mechanical analyzer which, as such, spawned other commercial systems.

II. TIME-TEMPERATURE-TRANSFORMATION (TTT) CURE DIAGRAM [10,21]

A general model for thermosetting materials which relates polymerization to properties has been developed. It arose from the ability of TBA experiments to distinguish between, and measure, the times to gelation and to vitrification. In this, a time-temperature-transformation (TTT) cure diagram relates the various states of matter encountered [i.e., liquid; sol/gel and gel rubber; sol, sol/gel and gel glass] to gelation and vitrification phenomena. The model is extended to rubber-modified thermosetting systems to show that a given chemical formulation can provide different morpholoiges through different cure procedures, and hence provide different material behavior. It is also extended to high temperature polymers where polymerization and degradation reactions compete. A kinetic equation which accounts for the change from liquid to glass in terms of both chemical and diffusion rate constants has been developed and used to calculate an extended isothermal TTT cure diagram for the reaction of a difunctional aromatic diglycidyl epoxy with a tetrafunctional aromatic diamine.

III. THE GLASS TRANSITION TEMPERATURE (T_g) AS AN INDEX FOR MONITORING CURE [21]

The TBA technique can readily measure the glass transition temperature of thermosetting systems from that of the unreacted formulation (T_{go}) to that of the fully cured system ($T_{g\infty}$) to within 0.5°C. Since T_g can change more than 200°C during cure, the TBA technique provides good resolution throughout the process of cure.

T_g is the principal parameter for thermosetting systems. Since T_g increases nonlinearly with conversion with T_g being related to conversion in a one-to-one manner, and is easily measured, it is a very useful and sensitive parameter for monitoring both the progress and properties of cure; furthermore, since vitrification is defined to occur when $T_g = T_{cure}$ (the temperature of cure), it is the basis of the vitrification contour in the time-temperature-transformation (TTT) cure diagram. The progress of cure in the TTT cure diagram can be documented as a series of iso-T_g contours: for epoxies prior to vitrification the reaction is kinetically chemically controlled; after vitrification the reaction becomes diffusion controlled. The basis for the one-to-one relationship between T_g and conversion is that all of the crosslinking sites are in effect trifunctional.

IV. ANOMALOUS BEHAVIOR OF THERMOSETTING POLYMERS: PROPERTIES AT ROOM TEMPERATURE VS. TIME AND TEMPERATURE OF CURE [8,15,20]

TBA and TP data show that the modulus in the glassy state (e.g., at 25°C) decreases with increased cure in spite of the increased crosslinking density. A summary of our investigations on the ramifications of this anomaly follows.

The room temperature density (ρ_{RT}) of a difunctional aromatic dpoxy resin cured with a tetrafunctional aromatic amine passes through a maximum value with increasing conversion. Cure results in a unique value of ρ_{RT} for each conversion as long as the material does not vitrify on cure. The occurrence of vitrification during cure eliminates the one-to-one relationship because of the non-equilibrium nature of the glass transition region and of the glassy state. Prolonged isothermal cure to well beyond vitrification results in limiting values of ρ_{RT} which decrease with increasing temperature of cure. The maximum in the ρ_{RT} vs. conversion relationship is explained in terms of 1) the effects on the free volume of shrinkage due to cure and of the corresponding increase in the glass transition temperature and 2) the effect of increasing average relaxation times in the vicinity of the glass transition with increasing T_g which affects the physical aging process on cooling through T_g. The effect of the anomalous behavior of density gives rise to parallel anomalous behavior in other material properties, for example in modulus, stresses in composites, and absorption of water.

V. PHYSICAL AGING OF THERMOSETTING SYSTEMS [18]

The current limitation to the quality of data in the TBA/TP technique is temperature control, which is currently to less than ± 0.1°C by using a large copper block. Data are excellent at a scale expansion of 30 times that of conventional presentation.

The sensitivity of the TP and TBA techniques is demonstrated by data on isothermal physical aging ("annealing") deep into the glassy state (i.e., Ta $<<$ T_g). For a fully cured epoxy system, the rate of annealing (as measured by the rate of change of modulus) is measurable and constant for a wide temperature range of more than 100°C between T_g and T_β ($T_\beta < T_g$). Perburbations in the thermomechanical behavior after annealing at Ta are restricted to a narrow range in the vicinity of Ta. A single specimen was used for successive annealing experiments (the effect of prior annealing was eliminated by heating to above T_g). Use of a single specimen provides an internal control for comparing the effects of aging versus the unaged specimen.

Comparison of physical aging at 50°C (i.e., $T_a << T_g$) vs. extent of cure for a high T_g liquid thermosetting dicyanate ester/polycyanurate system showed that in this system the rate of annealing decreased with increasing conversion (T_g) in spite of the initial modulus at 50°C decreasing with increased conversion (T_g). This showed that the free volume accessible for molecular relaxation decreases with increasing crosslinks in spite of the corresponding decrease in density.

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M. T. Aronhime and J. K. Gillham
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